PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
Mo-4981PCT		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US 00/ 19961	21/07/2000	23/07/1999
Applicant		
BAYER CORPORATION et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/19961

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C227/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 403 921 A (BAYER AG) 27 December 1990 (1990-12-27) page 4, line 21 -page 5, line 7; examples B1A-B1K	1-18
A	EP 0 816 326 A (BAYER AG) 7 January 1998 (1998-01-07) claims 1-8	1-18

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 October 2000	26/10/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hoffmann, K

Form PCT/ISA/210 (second sheet) (July 1992)

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0403921 A	27-12-1990	AT 113622 T	15-11-1994
		AU 623536 B	14-05-1992
		AU 5777990 A	03-01-1991
		BR 9002948 A	20-08-1991
		CA 2018803 A	23-12-1990
		DD 297982 A	30-01-1992
		DE 59007601 D	08-12-1994
		ES 2062188 T	16-12-1994
		JP 1930367 C	12-05-1995
		JP 3043472 A	25-02-1991
		JP 6053871 B	20-07-1994
		US 5126170 A	30-06-1992
		US 5236741 A	17-08-1993
EP 0816326 A	07-01-1998	DE 19717427 A	08-01-1998
		AT 192734 T	15-05-2000
		CA 2209131 A	02-01-1998
		DE 59701623 D	15-06-2000
		JP 10087583 A	07-04-1998
		US 5821326 A	13-10-1998

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

(PCT Rule 44.1)

To:
BAYER CORPORATION
Attn. ROY, Thomas W.
100 Bayer Road
Pittsburgh, PA 15205
UNITED STATES OF AMERICA

Date of mailing *(day/month/year)* 26/10/2000	
Applicant's or agent's file reference Mo-4981PCT	**FOR FURTHER ACTION** See paragraphs 1 and 4 below
International application No. PCT/US 00/ 19961	International filing date *(day/month/year)* 21/07/2000
Applicant BAYER CORPORATION et al.	

1. [X] The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:
The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Fascimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. [ ] The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. [ ] **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

[ ] the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

[ ] no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90*bis*.1 and 90*bis*.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Véronique Baillou

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international pbulication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When? Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How? Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped),whether

(i) the claim is unchanged;

(ii) the claim is cancelled;

(iii) the claim is new;

(iv) the claim replaces one or more claims as filed;

(v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."

2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."

3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."

4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international appplication is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

To:

ROY, Thomas, W.
Bayer Corporation
100 Bayer Road
Pittsburgh, PA 15205
ETATS-UNIS D'AMERIQUE

NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

Date of mailing (day/month/year) 20 November 2000 (20.11.00)	
Applicant's or agent's file reference Mo-4981PCT	**IMPORTANT NOTIFICATION**
International application No. PCT/US00/19961	International filing date (day/month/year) 21 July 2000 (21.07.00)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 23 July 1999 (23.07.99)
Applicant BAYER CORPORATION et al	

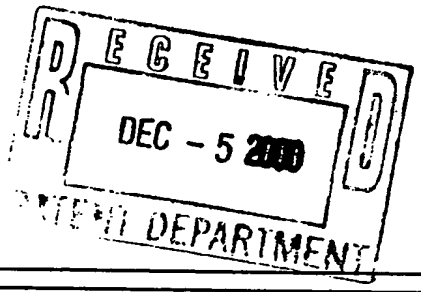
1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).

2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.

3. An **asterisk(*)** appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

4. The **letters "NR"** appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
23 July 1999 (23.07.99)	60/145,455	US	29 Augu 2000 (29.08.00)



The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

Marc Salzman

Telephone No. (41-22) 338.83.38

Form PCT/IB/304 (July 1998)

003669487

WO 01/07399
PCT/US00/19961

PATENT COOPERATION TREATY

PCT

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:
ROY, Thomas, W.
Bayer Corporation
100 Bayer Road
Pittsburgh, PA 15205
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 01 February 2001 (01.02.01)	
Applicant's or agent's file reference Mo-4981PCT	**IMPORTANT NOTICE**

International application No.	**International filing date** (day/month/year)	**Priority date** (day/month/year)
PCT/US00/19961	21 July 2000 (21.07.00)	23 July 1999 (23.07.99)

Applicant
BAYER CORPORATION et al

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
   AU,KP,KR,US

   In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
   AE,AG,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CN,CR,CU,CZ,DE,DK,DM,DZ,EA,EE,EP,ES,FI,
   GB,GD,GE,GH,GM,HR,HU,ID,IL,IN,IS,JP,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,MN,
   MW,MX,MZ,NO,NZ,OA,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,
   The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
   01 February 2001 (01.02.01) under No. WO 01/07399

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a **demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer J. Zahra
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

Form PCT/IB/308 (July 1996)

3796560

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
Mo-4981PCT		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US00/19961	21/07/2000	23/07/1999
International Patent Classification (IPC) or national classification and IPC C07C227/18		
Applicant BAYER CORPORATION et al.		

1. This International preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
16/01/2001	07.09.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Hoffmann, K Telephone No. +49 89 2399 8419

Form PCT/IPEA/409 (cover sheet) (January 1994)

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:
Description, pages:

1-11	as originally filed

Claims, No.:

1-18	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   - ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   - ☐ the language of publication of the international application (under Rule 48.3(b)).
   - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   - ☐ contained in the international application in written form.
   - ☐ filed together with the international application in computer readable form.
   - ☐ furnished subsequently to this Authority in written form.
   - ☐ furnished subsequently to this Authority in computer readable form.
   - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   - ☐ the description, pages:
   - ☐ the claims, Nos.:
   - ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-18
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-16
	No:	Claims	17,18
Industrial applicability (IA)	Yes:	Claims	1-18
	No:	Claims	

2. Citations and explanations
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re item V:

Reference is made to documents

D1: EP 0 403 921 A and

D2: EP 0 816 326 A .

None of the cited documents discloses a process according to independent claims 1 or 2 or to the mixture of polyaspartic esters of claim 17. The claimed subject-matter thus is deemed novel over the known prior art.

D1 refers to a method for preparing a single polyaspartic ester (examples A-K on page 7). In D2 a catalyst is used in said process. The applicant has shown in the examples that the process according to independent claims 1 or 9 is completed in a considerably shorter time in comparison to the process of D1. There is no known prior art which could give a hint to the skilled person to provide the process according to said claims. Thus the subject-matter of claims 1 and 9 and its dependent claims is deemed to involve an inventive step.

This is not the case for the products of claims 17 and 18. These products are a simple mixture of a polyaspartic ester prepared from a cyclic amine and a polyaspartic ester prepared from an acyclic amine. Examples for both kinds of esters are disclosed in D1. The skilled person would prepare a mixture of such esters without the ambit of any inventive skill. It thus appears that the subject-mater of claim 17 does not involve an inventive step.

Re item VIII:

According to claim 1 and page 6, lines 16-29 an excess of an ester of fumaric or maleic acid must be applied in step (a). The definitions of claims 5, 6, 9, 13 and 14, however, are not in agreement with this requirement.

Claim 13 is a simple repetition of the requirement in step (a) of claim 9 and is thus superfluous.

Claim 18 refers to the process of claim 17; claim 17, however, is a product claim. Furthermore, claim 18 simply repeats the features of claim 17. Thus this claim is superfluous.

In claims where a range is defined, the use of the word "about" casts doubt upon the scope of the claim (Article 6 PCT).

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference *(if desired) (12 characters maximum)* Mo-4981PCT

Box No. I TITLE OF INVENTION

IN-SITU PREPARATION OF POLYASPARTIC ESTER MIXTURE

Box No. II APPLICANT

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

BAYER CORPORATION
100 Bayer Road
Pittsburgh, PA 15205
United States of America

☐ This person is also inventor.

Telephone No.
(412) 777-2349

Facsimile No.
(412) 777-5449

Teleprinter No.

State *(that is, country)* of nationality: US

State *(that is, country)* of residence: US

This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

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This person is:

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☐ applicant and inventor

☐ inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality: US

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☐ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

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Box No.V DESIGNATION OF STATES

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Regional Patent

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☒ EA **Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT

☒ EP **European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT

☒ OA **OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT *(if other kind of protection or treatment desired, specify on dotted line)* .....

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Box No. VI PRIORITY CLAIM ☐ Further priority claims are indicated in the Supplemental Box.

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is: national application: country	regional application:* regional Office	international application: receiving Office
item (1) (23/07/1999)	60/145,455	US		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) *(only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office)* identified above as item(s): (1)

* *Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.*

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) *(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used)*: ISA / EPO

Request to use results of earlier search; reference to that search *(if an earlier search has been carried out by or requested from the International Searching Authority)*: Date *(day/month/year)* Number Country *(or regional Office)*

Box No. VIII CHECK LIST; LANGUAGE OF FILING

This international application contains the following **number of sheets**:

request	:	3
description (excluding sequence listing part)	:	11
claims	:	3
abstract	:	1
drawings	:	
sequence listing part of description	:	
Total number of sheets	:	18

This international application is **accompanied** by the item(s) marked below:

1. ☒ fee calculation sheet
2. ☒ separate signed power of attorney
3. ☐ copy of general power of attorney; reference number, if any:
4. ☐ statement explaining lack of signature
5. ☐ priority document(s) identified in Box No. VI as item(s):
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☐ other *(specify)*:

Figure of the drawings which should accompany the abstract:

Language of filing of the international application: ENGLISH

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Joseph C. Gil
Bayer Corporation
Vice President

For receiving Office use only

1. Date of actual receipt of the purported international application:
2. Drawings: ☐ received: ☐ not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:
4. Date of timely receipt of the required corrections under PCT Article 11(2):
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IN-SITU PREPARATION OF POLYASPARTIC ESTER MIXTURE

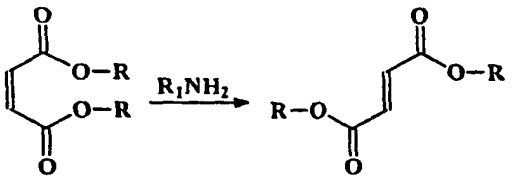
FIELD OF THE INVENTION

The invention relates to a method for making polyaspartic esters.

BACKGROUND OF THE INVENTION

Two-component coating compositions having a polyisocyanate component and an isocyanate-reactive component (a polyhydroxyl component) are known. These compositions are suitable for the preparation of high quality coatings that may be rendered rigid, elastic, resistant to abrasion and to solvents and, above, all, resistant to weathering. Polyaspartic esters have been used as isocyanate-reactive components in such two-component compositions. A polyaspartic ester can be used individually, with a polyisocyanate, or possibly in combination with polyols or polyamines. Alternatively, polyaspartic esters can be used with blocked polyamines such as ketimines, aldimines or oxizolidines.

Methods for making polyaspartic esters are known. It is known, for instance, that during the Michael Addition Reaction of an ester of fumaric or maleic acid and the primary amine, for instance, the ester of maleic or fumaric acid isomerizes to dialkyl fumarate in the presence of amines, according to the following chemical reaction:



The dialkyl fumarate is then converted to a polyaspartic ester. Mixtures of polyaspartic esters based on cyclic and acyclic amines have proven to be valuable isocyanate-reactive components of polyurea compositions that have found utility in the formulation of high solids coatings where solvent content is very low or zero. These formulations are used in architectural and automotive refinish applications. Known methods for preparing polyaspartic ester mixtures typically involve preparing polyaspartic esters

based on acyclic and cyclic amines separately and then combining each polyaspartic ester mixture. Polyaspartic esters based on acyclic amines, which contain amines attached to primary carbons, generally react with an isocyanate faster than polyaspartic esters based on cyclic amines that have an amine group attached to a secondary ring carbon. In addition, polyaspartic esters based on acyclic amines have a lower viscosity than polyaspartic esters based on cyclic amines. It is often desirable to blend these types of amines to achieve formulations with different viscosities and with intermediate reaction speeds.

U.S. Pat. No. 5,236,741 and U.S. Pat. No. 5,623,045 each disclose a single step process for the production of polyaspartic esters. Each process reacts an ester of maleic or fumaric acid with a primary polyamine such that preferably one olefinic double bond is present for each primary amino group. The patents teach that excess starting materials is removed by distillation after the reaction. Neither patent discusses how much time it takes for the reaction of the ester of maleic or fumaric acid to complete, i.e., to obtain a yield of about 100% of the polyaspartic ester. Neither patent addresses the issue of developing a process that makes a 100% yield of a mixture of (1) a polyaspartic ester based on a cyclic amine and (2) a polyaspartic ester based on an acyclic amine in a matter of days.

Unfortunately, such methods have prevented manufacturers of polyaspartic esters from delivering shipments to customers as quickly as would be desired. I have discovered that by following the teachings of the above-described known methods and using a 1:1 stoichiometric ratio, it takes several months to obtain full, or near-full, conversion of the reaction of a cyclic amine and an ester of maleic or fumaric acid. For instance, the use of bis (4-aminocyclohexyl)methane requires the polyaspartic ester to be stored in excess of six weeks to achieve 95% reaction and from six to twelve months to achieve complete reaction; and the use of bis (3-methyl-4-aminocyclohexyl)methane [commercially known as Laromin C-260] requires the polyaspartic ester to be stored in excess of eight weeks to achieve 95% reaction and from twelve to eighteen months to achieve 100% reaction. Removing excess ester of maleic or fumaric acid, as suggested by U.S. Pat. Nos. 5,236,741 and 5,623,045, is a time-consuming expensive procedure.

The problem of long waiting times has not been able to be resolved by making large amounts of the mixtures in advance because it is extremely difficult to predict customers' needs for the mixtures. Further, expensive storage, and inventory costs have discouraged the making and the storing of large amounts of the mixtures. As such, it is not uncommon for a customer to have to wait several months to receive an order of mixtures of polyaspartic esters.

It would be advantageous to develop an improved method for making mixtures of polyaspartic esters based on cyclic amines and polyaspartic esters based on acyclic amines that overcomes the above-named disadvantages.

SUMMARY OF THE INVENTION

The invention relates to a method for making a polyaspartic ester mixture *in-situ* comprising the sequential steps of (a) reacting a cyclic amine with an excess amount of an ester of fumaric or maleic acid to form a mixture containing first polyaspartic ester component and excess unreacted ester of fumaric or maleic acid, and (b) adding an acyclic amine to the mixture resulting from step (a) and reacting the acyclic amine with the excess ester of fumaric or maleic acid to form a second polyaspartic ester component. The invention is also directed to the in-situ mixture of polyaspartic ester esters formed during the method, prior to termination of the process, that contains the first polyaspartic ester component and the second polyaspartic ester component. The method makes it possible for customers to receive mixtures of the polyaspartic esters in a fraction of the time it has ordinarily taken. These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description and appended claims.

DETAILED DESCRIPTION OF THE INVENTION

As used in this application, the term "cyclic amine" refers to an amine that has at least one primary amine group attached to a cyclic group, e.g., an amine attached to a secondary ring carbon. The term "acyclic amine" refers to an amine that does not have a primary amine group attached to a cyclic.

The invention is based on the discovery that mixtures of polyaspartic esters based on cyclic amines and polyaspartic esters based on

acyclic amines can be prepared *in-situ*, (under certain conditions) in a fraction of the time it ordinarily takes to make them. It is critical that the cyclic amine first react with an excess ester of maleic or fumaric acid. As discussed below, if the sequence of the steps varies, e.g., if the steps are reversed or if the cyclic and acyclic amines are added simultaneously, the reaction proceeds substantially slower and is outside the scope of the present invention.

The first and second ester components are selected from esters of maleic acid and fumaric acid. Esters of maleic acid and fumaric acid include suitable dialkyl maleates or dialkyl fumarates. Suitable dialkyl maleates include, diethyl maleate, dipropyl maleate, dibutyl maleate, methyl propyl maleate, ethyl propyl maleate, and the like. Suitable dialkyl fumigates include, diethyl fumurate, dipropyl fumurate, dibutyl fumurate, methyl propyl fumurate, ethyl propyl fumurate, and the like. Generally, dimethyl maleate or dimethyl fumurate is not used in an appreciable amount because it has been discovered that these esters cause the precipitation of long needle-like crystals that no longer participate in the Michael Addition Reaction and that cause the reaction to stop altogether. It is believed that cinnamate esters do not react under the same reaction conditions as esters of maleic acid or fumaric acid.

The amine component is generally selected from difunctional or trifunctional cyclic and acyclic amines that can accomplish the objects of the invention. Suitable amines can be selected from the following. Suitable acyclic difunctional amines include but are not limited to ethylene diamine, 1,2-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 2,5-dimethylhexane, 2,2,4- and/or 2,4,4-trimethyl-1,6-diaminohexane, 1,11-diaminoundecane, 1,12-diaminododecane, 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, 2,4- and/or 2,6-hexahydrotolylenediamine, 2,4'- and/or 4,4'-diaminodicyclohexylmethane, and 3,3'-dimethyl-4,4'-diamino-dicyclohexylmethane. Suitable cyclic amines include aromatic polyamines such as 2,4- and/or 2,6-diaminotoluene, and 2,4'- and/or 4,4'-diaminodi-phenyl-methane are also suitable but less preferred. Other suitable cyclic amines include Bis- (3-methyl-4aminocyclohexyl) methane, 2,4-diamino-1-methyl, cyclohexane, and 2,6-diamino-1-methyl cyclohexane.

Suitable trifunctional amines include 4-aminomethyl-1,8-diaminooctane (also known as triaminononane supplied by Monsanto Company), tris-(2-aminoethyl)amine. It is believed that tetrafunctional amines, e.g., N,N,N',N'-tetrakis-(2-aminoethyl)-1,2-ethanediamine are also suitable.

The polyisocyanate component used to react with the polyaspartic ester mixtures includes any polyisocyanate, which when used in accordance with the invention, meets the object of the invention. Suitable polyisocyanates for use as polyisocyanate component in accordance with the present invention include the known polyisocyanates of polyurethane chemistry. Examples of suitable low molecular weight polyisocyanates having a molecular weight of 168 to 300 include 1,4-diisocyanatobutane, 1,6-hexamethylene diisocyanate, 2,2,4- and/or 2,4,4-trimethyl-1,6-hexamethylene diisocyanate, dodecamethylene diisocyanate, 1,4-diisocyanatocyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI), 2,4'- and/or 4,4'-diisocyanato-dicyclohexyl methane, 2,4- and/or 4,4'-diisocyanatodiphenyl methane and mixtures of these isomers with their higher homologues that are obtained in a known manner by the phosgenation of aniline/formaldehyde condenses, 2,4- and/or 2,6-diisocyanatotoluene and any mixtures of these compounds. Preferred cyclic isocyanates include diphenylmethane 4,4'-diisocyanate (MDI), diphenylmethane 2,4'-diisocyanate, 2,4- and/or 2,6-diisocyanatotoluene. Preferred aliphatic isocyanates include hexamethylene diisocyanate, isophorone diisocyanate, 2,4'- and/or 4,4'-diisocyanato-dicyclohexyl methane.

Additional suitable polyisocyanate components include derivatives of the above-mentioned monomeric polyisocyanates, as is conventional in coatings technology. These derivatives include polyisocyanates containing biuret groups as described, for example, in U.S. Pat. Nos. 3,124,605 and 3,201,372 and DE-OS 1,101,394, incorporated herein by reference in their entirety; polyisocyanates containing isocyanurate groups as described in U.S. Pat. No. 3,001,973, DE-PS 1,022,789, 1,222,067 and 1,027,394 and DE-OS 1,929,034 and 2,004,048, incorporated herein by reference in their entirety; polyisocyanates containing urethane groups as described, for instance, in DE-OS 953,012, BE-PS 752,261 and U.S. Pat. Nos. 3,394,164 and 3,644,457; polyisocyanates containing carbodiimide

groups as described in DE-PS 1,092,007, U.S. Pat. No. 3,152,162 and DE-OS 2,504,400, 2,537,685 and 2,552,350, incorporated herein by reference in their entirety; and polyisocyanates containing allophanate groups as described, for example, in GB-PS 994,890, BE-PS 761,626 and NL-OS 7,102,524. Suitable polyisocyanates also include polyisocyanates that contain uretdione groups. In one embodiment, asymmetric trimers such as those in U.S. Pat. No. 5,717,091, incorporated herein by reference in its entirety. Isocyanate group-containing prepolymers and semi-prepolymers based on polyisocyanates can also be used as the polyisocyanate component. These prepolymers and semi-prepolymers generally have an isocyanate content ranging from about 0.5 to 30% by weight, preferably about 1 to 20% by weight, and are prepared in a known manner by the reaction of starting materials, e.g., isocyanate-reactive compounds such as polyols, at an NCO/OH equivalent ratio of about 1.05:1 to 10:1, preferably about 1.1:1 to 3:1.

The first step of the process involves reacting a cyclic amine with an excess amount of an ester of fumaric or maleic acid to form a mixture containing first polyaspartic ester component and excess unreacted ester of fumaric or maleic acid. The equivalent ratio of the ester of maleic or fumaric acid to the cyclic polyamine is greater than 1:1, preferably 1.2:1 to 5:1 and more preferably 1.4:1 to 3:1. Generally, the more excess ester of maleic or fumaric acid used, the faster the initial reaction proceeds. To obtain a yield that is about 100% at a ratio of ester of maleic or fumaric acid to cyclic amine of 2:1, for instance, the reaction lasts less than 24 hours. When the number ratio of ester of maleic or fumaric acid to cyclic amine of 5:1, for instance, the reaction lasts less than 8 hours. It is generally preferred to have the initial reaction to be complete in about eight hours. Actual ratios for a specific application can be determined by routine experimentation.

The second step of the process involves adding an acyclic amine to the mixture and reacting the acyclic amine with the excess ester of fumaric or maleic acid to form a second polyaspartic ester component. The acyclic amine is preferably used in an amount that corresponds to the excess, unreacted ester of fumaric or maleic acid. Accordingly, the equivalent ratio of acyclic amine to cyclic amine is preferably 0.2:1 to 4:1,

preferably 0.4:1 to 2:1. The reaction of the excess ester of maleic or fumaric acid and the acyclic amine generally takes less than two weeks.

The reaction conditions at which the method is carried out under are discussed below. Generally, the reaction takes place at a temperature of 0 to 100°C. The reaction may take place in the absence or in the presence of suitable solvents such as methanol, ethanol, propanol, ethyl- or butyl acetate and mixtures of these solvents. The pressure of the reaction is generally atmospheric. As such, since the reaction of the cyclic polyamine and the ester of maleic or fumaric acid lasts hours instead of months, conversions of about 100% of mixtures of the polyaspartic ester based on the cyclic amine and the polyaspartic ester based on the acyclic amine can be obtained in days instead of months. Generally, a conversion of about 100% is obtained in less than 10 to 14 days.

The polyaspartic ester mixtures can be used in applications such as coatings. The low viscosity allows the formulation of paint at high or very high solids, or even paint with no solvent. Coatings applications can use polyurea coatings based on polyaspartic esters and polyisocyanates include general factory applied coating and field applied architectural or automotive refinish coatings.

The invention will now be described in the following illustrative examples. All percentages given are by weight unless otherwise indicated.

EXAMPLE 1

A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 75.6 g (0.720 eq) bis *p*-aminocyclohexyl methane (PACM) was admitted to the flask. 348.7 g (2.024 eq) diethyl maleate was admitted to the flask via the addition funnel over a one hour period. The temperature of the reaction mixture rose to 60°C as a result of a reaction exotherm. The temperature was maintained at 60°C for an additional five hours. The unsaturation number was 35.7 mg maleic acid per gram of resin, which indicated 100% of the PACM had been converted to aspartate. 75.6 g (1.304 eq) 1,6-hexanediamine was added to the reaction over a forty-five minute period. The reaction was heated at 60°C for four hours when the unsaturation number was 1.05, which indicated

the reaction was 97% complete. One week later the unsaturation number was 0, which indicated the reaction was 100% complete.

To determine the extent of the reaction, the unsaturation number was determined by a thiol-iodine titrametric method. This method titrates all double bonds so that the sum of both maleic and fumaric esters is included in the resultant unsaturation number. The units of unsaturation number is given in terms of milligrams maleic acid per gram of resin. Twenty-four hours later the unsaturation number was 0.66, which indicated the reaction was 98% complete.

The thiol-iodine titrametric method involved the following steps: (1) dissolving a sample in 10 ml pyridine in 100 ml flask, (2) adding 5 drops 1% solution of phenothalein indicator in ethanol, (3) dispensing 8 ml 1 N solution of 1-dodecanethiol in ethanol, (4) titrating with 0.5 N solution of sodium hydroxide in ethanol until deep purple color is achieved. (The timer was started for exactly two minutes at first contact of NaOH/ethanol solution), (5) adding 2 ml glacial acetic acid after two minutes, (6) adding 60 ml ethanol, (7) titrating with 0.1 N iodine aqueous solution until a persistent yellow color was observed, and (8) running blank with every set of titrations, and (9) calculating the maleic acid number. A nitrogen blanket was provided for steps 2 through 4.

Calculations were made in accordance to the following formula:

$$\text{maleic acid number (mg per g resin)} = \frac{(\text{blank volume} - \text{sample volume})\ 1.161}{\text{sample weight}}$$

COMPARATIVE EXAMPLE A

This example demonstrates the difference between Sequential of Example 1 and the reverse order of sequential mixing PACM and HDA). The procedure of Example 1 was repeated as follows. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 50.0 g (0.862 eq) 1,6-hexanediamine (HDA) was admitted to the flask. 230.1 g (1.338 eq) diethyl maleate was admitted to the flask via the addition funnel over a one and one half hour period. The temperature of

the reaction mixture rose to 60°C as a result of a reaction exotherm. The temperature was maintained at 60°C for an additional four and one half hours. The unsaturation number was 20.0 mg maleic acid per gram of resin, which indicated 99.8 % of the HDA had been converted to aspartate.

50.0 g (.862 eq) bis *p*-aminocyclohexyl methane (PACM) was added to the reaction over a thirty minute period. The reaction was heated at 45°C for four and one half hours when the unsaturation number was 11.44, which indicated the reaction with PACM was 42 % complete. At the end of one week the unsaturation number was 5.05, which indicated the reaction with PACM was only 75 %complete. At the end of one month the unsaturation number was 1.95, which indicated the reaction was only 90% complete.

COMPARATIVE EXAMPLE B

This example demonstrates the difference between sequential process Example 1 and concurrent mixing of PACM and HDA. The procedure of Example 1 was repeated as follows. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 50.0 g (0.476 eq) PACM and 50.0 g (0.862 eq) 1,6-hexanediamine was admitted to the flask at 40°C and mixed for five minutes. 230.1 (1.338 eq) diethyl maleate was admitted to the flask via the addition funnel over a two hour period. The temperature of the reaction mixture rose to 60°C as a result of a reaction exotherm. The reaction was held at 60°C for an additional four hours. The unsaturation number was 15.82 mg maleic acid per gram of resin, which indicated 84.0 % of the maleate had been converted to aspartate. If it is assumed that 90 % of the hexanediamine had been converted, this means that only 23 % of the PACM had been converted. After one month the unsaturation number was 1.83, which indicated 94 % of the maleate had been converted to aspartate. If it is assumed that 100 % of the hexanediamine had been converted, this means that only 89 % of the PACM had been converted after one month.

EXAMPLE 2

The procedure of Example 1 was repeated as follows. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and

nitrogen inlet. 50.0 g (0.476 eq) bis *p*-aminocyclohexyl methane (PACM) was admitted to the flask. 230.1 g (1.338 eq) diethyl maleate was admitted to the flask via the addition funnel over a one and one half hour period. The temperature of the reaction mixture rose to 40°C as a result of a reaction exotherm. The temperature was maintained at 40°C for an additional four and one half hours. The unsaturation number was 36.0 mg maleic acid per gram of resin, which indicated 99.5 % of the PACM had been converted to aspartate.

50.0 g (.862 eq) 2-methyl-1,5-pentane diamine (available from DuPont as Dytek A) was added to the reaction over a forty-five minute period. The reaction was heated at 45°C for four and one half hours when the unsaturation number was 4.87, which indicated the reaction was 87 % complete. At the end of one week the unsaturation number was zero, which indicated the reaction was complete.

COMPARATIVE EXAMPLE C

The procedure of Example 2 was repeated as follows. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 150.0 g (1.43 eq) PACM and 150.0 g 2-methyl-pentane-diamine (Dytek A, available from Dupont) were admitted to the flask and mixed for five minutes. 689.7 g (4.01 eq) diethyl maleate was admitted to the flask via the addition funnel over a one hour period. The temperature of the reaction mixture rose to 60°C as a result of a reaction exotherm. The reaction was held at 60°C for an additional five and one half hours. The unsaturation number was 4.35 mg maleic acid per gram of resin, which indicated 90.7% of the maleate had been converted to aspartate. If it is assumed that 95% of the 2-methylpentane-diamine had been converted, this means that only 83% of the PACM had been converted.

After 11 days, the unsaturation number was 1.52, which indicated 96.8% of the maleate had been converted to aspartate. If it is assumed that 100% of the 2-methylpentane-diamine had been converted, this means that only 90.1% of the PACM had been converted after 11 days. After 18 days, the unsaturation number was 0.43, which indicated 99.1% of the maleate had been converted to aspartate. If it is assumed that 100% of the 2-methylpentane-diamine had been converted, this means that 97.4% of the PACM had been converted after 18 days.

The conversion of PACM to aspartate occurred at about the same rate as if the Dytek were not present.

COMPARATIVE EXAMPLE D

This example demonstrates the difference between the sequential process of Example 2 and the reverse order of sequential mixing PACM and Dytek A. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 50.0 g (0.862 eq) 2-methyl-1,5-pentane diamine (available from DuPont as Dytek A) was admitted to the flask. 230.1 g (1.338 eq) diethyl maleate was admitted to the flask via the addition funnel over a one and one half hour period. The temperature of the reaction mixture rose to 60°C as a result of a reaction exotherm. The temperature was maintained at 60°C for an additional four and one half hours. The unsaturation number was 19.6 mg maleic acid per gram of resin, which indicated 100 % of the HDA had been converted to aspartate. 50.0 g (.862 eq) bis *p*-aminocyclohexyl methane (PACM) was added to the reaction over a thirty minute period. The reaction was heated at 45°C for four and one half hours when the unsaturation number was 12.26, which indicated the reaction with PACM was 37 % complete. At the end of one week the unsaturation number was 4.17, which indicated the reaction with PACM was only 79 %complete. At the end of one month the unsaturation number was 1.92, which indicated the reaction was only 90% complete.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

WHAT IS CLAIMED IS:

1. A method for making a polyaspartic ester mixture in-situ comprising the sequential steps of:

(a) reacting a cyclic amine with an excess amount of an ester of fumaric or maleic acid to form a mixture containing a first polyaspartic ester component and excess unreacted ester of fumaric or maleic acid, and

(b) adding an acyclic amine to the mixture resulting from step (a) in an amount sufficient to react the acyclic amine with the excess ester of fumaric or maleic acid and to form a second polyaspartic ester component.

2. The method of Claim 1, wherein the cyclic amine comprises a component selected from the group consisting of 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, hexahydro-2,4- diaminotoluene, hexahydro-2,6-diaminotoluene, alkyl substituted cyclohexanediamines 2,4'- and/or 4,4'-diamino-dicyclo-hexylmethane, 3,3'-dimethyl-4,4'-diaminodicyclohexyl-methane, isomers of diaminodicyclohexylmethane having a methyl group as a substituent, and 3,4-aminomethyl-1-methylcyclohexylamine.

3. The method of Claim 1, wherein the acyclic amine comprises a component selected from the group consisting of ethylene diamine, 1,2-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 2-methyl-1,5-diaminopentane, 2,5-diamino-2,5-dimethylhexane, 2,2,4-trimethyl-1,6-diaminohexane, 2,4,4-trimethyl-1,6-diaminohexane, 1,11-diaminoundecane, and 1,1,2-diaminododecane.

4. The method of Claim 1, wherein the ester of fumaric or maleic acid comprises an ester selected from the group consisting of diethyl maleate, dipropyl maleate, dibutyl maleate, methyl propyl maleate, ethyl propyl maleate, diethyl fumurate, dipropyl fumurate, dibutyl fumurate, methyl propyl fumurate, and ethyl propyl fumurate.

5. The method of Claim 1, wherein the number ratio of the cyclic amine to the ester of fumaric or maleic acid is at least 2:1.

6. The method of Claim 1, wherein the number ratio of the cyclic amine to the ester of fumaric or maleic acid is from about 20:1 to about 2:1.

7. The method of Claim 1, wherein a conversion of about 100% of the first and second polyaspartic ester components is obtained in less than 20 days.

8. The method of Claim 1, wherein a conversion of about 100% of the first and second polyaspartic ester components is obtained in less than 8 days.

9. A method for making a polyaspartic ester mixture in-situ comprising the sequential steps of:

(a) reacting a cyclic amine with an ester of fumaric or maleic acid to form a mixture containing a first polyaspartic ester component and excess unreacted ester of fumaric or maleic acid, wherein the number ratio of the cyclic amine to the ester of fumaric or maleic acid is at least 2:1 and

(b) adding an acyclic amine to the mixture resulting from step (a) and reacting the acyclic amine with the excess ester of fumaric or maleic acid to form a second polyaspartic ester component, wherein a conversion of about 100% of the first and second polyaspartic ester components is obtained in less than 20 days.

10. The method of Claim 9, wherein the cyclic amine comprises a component selected from the group consisting of 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, hexahydro-2,4- diaminotoluene, hexahydro-2,6-diaminotoluene, alkyl substituted cyclohexanediamines 2,4'- and/or 4,4'-diamino-dicyclo-hexylmethane, 3,3'-dimethyl-4,4'-diaminodicyclohexyl-methane, isomers of diaminodicyclohexylmethane having a methyl group as a substituent, and 3,4-aminomethyl-1-methylcyclohexylamine.

11. The method of Claim 9, wherein the acyclic amine comprises a component selected from the group consisting of ethylene diamine, 1,2-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 2-methyl-1,5-diaminopentane, 2,5-diamino-2,5-dimethylhexane, 2,2,4-trimethyl-1,6-

diaminohexane, 2,4,4-trimethyl-1,6-diaminohexane, 1,11-diaminoundecane, and 1,1,2-diaminododecane.

12. The method of Claim 9, wherein the ester of fumaric or maleic acid comprises an ester selected from the group consisting of symmetrical esters, and asymmetrical esters.

13. The method of Claim 9, wherein the number ratio of the cyclic amine to the ester of fumaric or maleic acid is at least 2:1.

14. The method of Claim 9, wherein the number ratio of the cyclic amine to the ester of fumaric or maleic acid is from about 20:1 to about 2:1.

15. The method of Claim 9, wherein a conversion of about 100% of the first and second polyaspartic ester components is obtained in less than 20 days.

16. The method of Claim 9, wherein a conversion of about 100% of the first and second polyaspartic ester components is obtained in less than 8 days.

17. An in-situ mixture of polyaspartic ester esters formed during the method of Claim 9, prior to termination of the process, comprising the first polyaspartic ester component and the second polyaspartic ester component.

18. An in-situ mixture of polyaspartic ester esters formed during the method of Claim 17, prior to termination of the process, comprising the first polyaspartic ester component and the second polyaspartic ester component.

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(54) Title: IN-SITU PREPARATION OF POLYASPARTIC ESTER MIXTURE

(57) Abstract: A method for making a polyaspartic ester mixture *in-situ* comprising the sequential steps of (a) reacting a cyclic amine with an excess amount of an ester of fumaric or maleic acid to form a mixture containing first polyaspartic ester component and excess unreacted ester of fumaric or maleic acid, and (b) adding an acyclic amine to the mixture resulting from step (a) and reacting the acyclic amine with the excess ester of fumaric or maleic acid to form a second polyaspartic ester component.